



Energy, Mines and
Resources Canada

Énergie, Mines et
Ressources Canada

CANMET

Canada Centre
for Mineral
and Energy
Technology

Centre canadien
de la technologie
des minéraux
et de l'énergie

CALIBRATION METHODOLOGY AND QUALITY CONTROL IN THE URANIUM ANALYTICAL LABORATORY

J.L. Dalton
Chemical Laboratory

January 1987

Project: 30.69.02
Analytical Methodology

This document is an interim

interim report prepared for the

technical and scientific

community for use as a

reference document

the opinion of the author

for Mineral and Energy Technology

(CANMET)

Ce document est un rapport

interim préparé et rédigé

pour la communauté

technique et scientifique

en tant que document

de référence

à l'usage du Centre canadien de

technologie des minéraux et de

l'énergie (CANMET)

14 pp

MINERAL SCIENCES LABORATORIES
DIVISION REPORT MSL 87-2 (TR)

MICROMEDIA

CALIBRATION METHODOLOGY AND QUALITY CONTROL
IN THE URANIUM ANALYTICAL LABORATORY

by

J.L. Dalton*

ABSTRACT

The Division of Nuclear Fuel Cycle of the International Atomic Energy Agency requested the assistance of CANMET in the preparation of a manual on the analytical chemistry in the uranium industry. The staff of the Chemical Laboratory has responded to this request and this report, which deals with some aspects of analytical methodology and quality control, is intended to be part of this manual.

Key Words: Analysis, Management, Calibration, Quality Control

* Section Head, XRF and Radioanalysis Section, Chemical Laboratory, Mineral Sciences Laboratories

MÉTHODE DE CALIBRATION ET CONTRÔLE DE LA QUALITÉ
AU LABORATOIRE DE L'ANALYSE DE L'URANIUM

par

J.L. Dalton*

RÉSUMÉ

La Division du cycle du combustible nucléaire de l'Agence internationale de l'énergie atomique a demandé à CANMET de l'aider à rédiger un manuel sur la chimie analytique dans l'industrie de l'uranium. Le personnel du Laboratoire de chimie a répondu à cette demande et le présent rapport, qui porte sur certains aspects de la méthode d'analyse et de contrôle de la qualité, doit être intégré au manuel.

Mots clés: Analyse, Gestion, Calibration, Contrôle de la qualité

* Chef de section, Section de FX radiométrie et fluorimétrie,
Laboratoire de chimie, Laboratoires des sciences minérales

CALIBRATION METHODOLOGY AND QUALITY CONTROL
IN THE URANIUM ANALYTICAL LABORATORY

This chapter deals with the calibration methodology and quality control programs that may be used in the analytical laboratory. The following text is more relevant to the mine/mill control than to the geological survey aspect.

For industrial calibration, the ideal method is to use calibration materials that are identical to the sample being analyzed. The simplest way to prepare in-house calibration materials is to collect several samples of each type, have these blended, homogenized and subsequently analyzed by a reputable laboratory, or preferably several laboratories. These materials may then be used for calibration purposes if they are reasonably stable. However, if it is desired to analyse these materials in the site laboratory, one must take into account the peculiarities of the ore-body. Most ore-bodies have sufficient unique features to demand attention from the analyst with respect to the presence of possible interferences and the extent of acid solubility.

The solubility of an element in a particular ore-body should be verified by dissolution tests varying from simple to the most stringent in order to determine which procedure is suitable for the control process and the geological survey requirements. For these two end uses, it may not be necessary to use the same type of dissolution procedure on a continuing day-to-day basis as that required by a theoretical scientific study. However, it is important to know the extent to which a given dissolution procedure will dissolve different elements. For uranium, this may be as simple as comparing results obtained directly on the solid material by the delayed neutron counting method with those obtained after various dissolution tests. These would probably vary from a cold single-acid leach to a hot multiple acid leach, taken to dryness, followed by an appropriate fusion on any resultant acid-insoluble residue.

The techniques of internal standard and standard addition are applicable in analytical work when the composition of the sample and the approximate analyte concentration are unknown, and in which a direct comparison with certified reference materials (CRM), pure compounds, or with single or multi-component calibrations solutions is impractical.

Calibration by the use of an internal standard, involves the addition of a relatively large amount of the internal standard element to the sample and is best done with solutions. The choice of a suitable element to use as an internal standard must consider the compatibility with the matrix, the optimum concentration which enables precise measurement and the chemical and physical properties of the internal standard element with respect to the properties of the analyte. Moreover, the intensity of the internal standard element must be affected by matrix change in exactly the same manner as the analyte intensity. These changes are caused by the chemical and physical properties of the sample. The sample undergoing analysis must also be free, or contain very little of the standard addition element.

Calibration by this method can be rapid and convenient. An example is the determination of uranium in solution by X-ray fluorescence (XRF) analysis. A small measured quantity of the internal standard solution 0.1 mL, is added to 5.0 mL of the solution, the uranium and bromine XRF measurements are made and a uranium/bromine ratio is calculated from the net intensities. This ratio is then divided by that of the uranium standard solution to obtain the analytical result. If the internal standard calibration results are plotted, the ordinate is the ratio of the net analyte to internal standard intensities and the abscissa is the concentration axis.

The choice of internal standard element is often restricted by the composition of the solution. The presence of certain elements may cause a precipitate to form upon addition of the internal standard. For example, halogens cannot be used with solutions containing silver, alkaline earths form precipitates with sulphate, phosphate and bismuth precipitates in the presence of hydrochloric acid. Examples of internal standard calibration are the use of palladium and cobalt in optical emission spectrometry (1), and bromine, strontium and lead in X-ray spectrometry (2). The use of internal standards in X-ray spectrometry is discussed by Bertin (3).

As mentioned previously, the internal standard method is best applied to solutions but powders can also be analyzed using this method, albeit with

some care, by X-ray spectrometry. The internal standard is mixed intimately with the sample in order to obtain a homogeneous mixture. If a shatter-box or other robust device is used for mixing, there may be a grinding effect and a consequent change in the grain size distribution of the mixture, with respect to the original sample. At a later stage, experience may show that the internal standard is not necessary for a particular analysis but in order to continue using the existing calibration, it will be necessary to continue with all the sample preparation steps because the XRF intensities are a function of the grain-size distribution.

Internal standard calibration may be used conveniently when preparing fused glass discs for X-ray spectrometry. For this work, the internal standard is simply added to the sample and the flux before the fusion step.

The standard addition method differs from the internal standard method in that the element being determined is the element that is added. Although standard addition is usually carried out on solutions, it can easily be applied in the preparation of fused glass discs but requires care if the direct use of solids is involved. The same comments with respect to grain size distribution that were mentioned previously in the discussion of the internal standard method apply to the standard addition method when used for X-ray spectrometric analysis. When the method is applied to sample solutions, usually 3 or 4 identical aliquots of the solution are taken and increasing volumes of a standard solution of suitable concentration are added. Typically, the final concentration of the analyte in the resulting solutions would be about 0.5, 1.5, and 2 times the concentration of the analyte in the sample solution. Care must be exercised in the intensity measurement because it is very important that the background measurement does not reflect the intensities of the added analyte. Small errors in the background measurement may influence the slope of the calibration plot. Data from a hypothetical determination using the standard addition technique are given in Table 1 and plotted in Fig. 1. The abscissa is plotted in terms of analyte added. Consequently, the volumes of the standard analyte solution added must be exact and the final volumes of the solutions must be the same. When making the additions of standard analyte solution, it is important to maintain the same acid concentration in the resultant solutions as in the analyte solution.

In favourable cases, or after the analysis of a relatively large number of samples, it may be observed that the slope of the calibration plot is constant, within analytical error. In these situations, it will not be necessary to make the additions and the slope may then be applied directly to the sample data to obtain the analyte concentrations. This is particularly useful in the case of powders analysis. However, it is advisable to check periodically the slope by the standard addition method.

Direct comparison between sample and standard is often carried out in measurement techniques such as atomic-absorption and flame-emission spectrometry, the various types of optical emission spectrometry and in X-ray fluorescence analysis. Care must be taken to ensure that the sample and standard are of a similar composition, including acid type and strength and that the concentration of analyte in the sample is within the range of the calibration standard. Extrapolation of the calibration curve may lead to serious error. Care must also be taken to ensure that any interferences present are detected and that corrective action is taken. Direct comparison is recommended in many of the methods described in the monograph by Donaldson (4).

Certified reference materials are powdered ores, rocks, slags and metals and alloys which have been prepared, analyzed and documented for use in analytical laboratories. They are invaluable in the laboratory for a variety of purposes such as calibration, quality-control, preparation of in-house control materials and methodology comparisons. They provide a benchmark for the analytical industry and should be used frequently.

There are many organizations which prepare and sell CRMs (5). Most of these are government departments or institutions, but some are also private companies. The geological materials chosen for CRMs are representative of ores and rocks from around the world and may, in favourable cases, have similarities to the chemical composition of a particular ore-body of interest to the laboratory. In certain cases, a CRM may be certified only for its uranium content as with some from the International Atomic Energy Agency (IAEA) (6) and Canadian Certified Reference Materials Project (CCRMP) (7), while in other cases several

elements may be certified and additional analytical information is available on the remaining elements (7).

The preparation of certified material generally involves a large number of laboratories in order to reach consensus values. It is beneficial for a laboratory to participate in these programmes because it provides an opportunity to compare accuracy and precision, and also, the laboratory's reputation may be enhanced by participation.

Quality control is a process whereby standard solutions and/or reference materials are analyzed concurrently with the sample to determine and document the accuracy of the various determinations. The reference solution or material must be subjected to exactly the same procedural and measurement steps that the sample receives to ensure that the whole method is checked. Without quality control the results obtained are directly dependent on the vagaries of the analyst, laboratory services and instruments. Quality control work often provokes considerable discussion however, because it is expensive, time-consuming and increases the analytical work-load. However, this work is the only way in which an analytical laboratory can realistically assign accuracy statements to analytical work produced during normal laboratory operation. Although the accuracy of an analytical method can be calculated, the assignment of these same figures to the control laboratory can be quite misleading. The accuracy associated with a method was probably accumulated over a lengthy period of time and special care was used during the manipulative and measurement operations. In the control laboratory, there are often pressing demands for rapid turn-around time and the idiosyncracies of industrial shift work.

There is an important human consideration that must be continually borne in the minds of the supervisory staff of the analytical laboratory. The purpose of the quality control program is to monitor the performance of a whole method, not only the operator. Supervisory staff must not create the impression that the purpose of the program is to harass the staff. When quality control results indicate methodology problems, the whole method is suspect, not just the analyst. A quality control program can define when problems occur, if results go awry, and what analytical results might be suspect. The quality control operation is particularly important when

staff changes frequently or when a periodic staff rotation system exists in the laboratory.

The choice of materials for a quality control program is very important. They must be similar in composition and physical properties to the samples undergoing analysis, be stable for a relatively long time and sufficiently well characterized to permit a reasonable assessment of accuracy and precision to the analytical work. For example, material containing a high concentration of iron would not be used as a quality control sample for uranium determination by optical fluorimetry, even though it contained an appropriate quantity of uranium, if a better material was available. The preparation of control materials can range from simple and inexpensive to complex and expensive. A representative sample from a particular type of analysis, mill heads, for example, may be used as a control sample if one has a reasonably good supply and it is stable for a reasonable length of time. Similarly single or multi-element calibration solutions may also be used, care being made to match acid strength and type between standard and sample. These can be prepared in the laboratory at relatively low cost. The disadvantage to their use is that these materials do not have any documentation outside the particular laboratory. If results are circulated outside the organization, it is best to use control materials that have been analyzed by a reputable laboratory. However, if it is desired to supply control documentation which has important ramifications, such as the sale of product, then it is best to use internationally-accepted CRMs, even though the use of these materials is expensive if used frequently. In-house control materials may be used most of the time, but the certified reference materials should be used in important cases and periodically to monitor results obtained when using in-house materials.

The amount of control work necessary is a contentious issue. The control limits, that is the maximum deviation from the true value that can be tolerated by the appropriate industrial process, should be decided upon by discussion between laboratory management and the end-user of the results. These limits must be achievable in the laboratory and the associated cost of complying with the end-user's requests should become an integral part of that particular production cost. Once control limits have been established, the amount of quality control analysis should be decided

by laboratory management. If the variability of the results obtained by the method approaches the established control limits, then the amount of control work may be large, e.g. 20% or one sample in five is a control sample. Conversely, if the control limits are well removed from that of the method variability, then the control work will only be a small fraction of the work-load, say one control sample for every twenty analytical samples. However, there may be special circumstances where it is necessary to analyze a few samples at a time, for example aqueous solutions from the barium chloride treatment pond requiring radium-226 determination. In this case, it would be necessary to have a radium-226 control solution and a reagent blank analyzed concurrently with the few solutions. If the concentrations of the analytes in the solutions to be analyzed are near the detection limit of the method, the concentrations in the control samples should be sufficiently higher than the detection limit to permit an accurate measurement. Reagent blanks should be analyzed as well to check on the intercept value of the calibration curve and for possible contamination from the laboratory glassware. The statistical aspects of experimental and industrial measurement are discussed in the NBS Handbook by Natrella (8) and the ASTM Manual on Quality Control of Materials (9).

There are several ways in which control samples may be inserted into the work load. The easiest is simply for the supervisor to give the control sample to the technical staff and ask for one control sample analysis per certain number of samples. The disadvantage with this approach is that the staff may be more careful with this sample than with others, knowing that the supervisor will be scrutinizing the result. The advantage is that technical staff and the supervisor know immediately whether or not the results are acceptable. The technical staff may also be asked to chart control sample results on a continuing basis, thus providing some self-motivation to work carefully as the chart will be a visual presentation of work quality, especially if the plot shows the results of just a single worker.

On the other hand, the control sample may be inserted into the work load by management, labelled as a management sample and the results are reported directly to management. The supervisor may or may not be aware of the concentration(s) in the control sample, or even that the sample is a

control sample. The advantage with this approach is that the control sample is truly an unknown. The disadvantage, again is that the staff will be very careful with this sample. An alternative to this approach is to ask the end-user of the analytical services to submit the control samples with the normal work-load and inform management of the laboratory number assigned to the control sample. Management would have to refer to the end-users report to ascertain the accuracy of the analytical work on the control sample.

As mentioned previously, the purpose of the quality control program is to document the accuracy of analytical work during normal operations. A necessary part of this program involves suitable recording of the results of the control work. If a worksheet or notebook system for recording the analytical work is used in the laboratory, then the results obtained for the control sample will be readily available along with the pertinent sample results. If a computer-based management system is used, however, some effort will be required to ensure that the control sample data are entered into the data base together with the relevant sample data and that both sets of data can be retrieved at the same time.

REFERENCES

1. Personal Communication, R.H. Horton to J.L. Dalton CANMET, Energy, Mines and Resources, Canada, Ottawa.
2. J.L. Dalton, Unpublished Results, CANMET, Energy, Mines and Resources, Canada, Ottawa.
3. E.P. Bertin, Principles and Practice of X-Ray Spectrometric Analysis, ISBN 0-306-30809-6, Plenum Press, New York.
4. E.M. Donaldson, Methods for the Analysis of Ores, Rocks and Related Materials, Monograph 881 Second Edition, CANMET, Energy Mines and Resources, Canada, Ottawa.
5. ISO/REMCO Directory 1982, ISO Central Secretariat, Case Postale 56, CH-1211, Genève 20, Switzerland.
6. Analytical Quality Control Services, Laboratory Seibersdorf, International Atomic Energy Agency, Vienna, Austria.
7. Canadian Certified Reference Materials Project, CANMET, Energy, Mines and Resources, Canada.
8. M.G. Natrella, Experimental Statistics, Handbook 91, United States Department of Commerce National Bureau of Standards, Washington D.C.
9. ASTM Manual on Quality Control of Materials, American Society for Testing Materials, Philadelphia.

TABLE 1

Standard Addition Data

Sample solution estimated value 0.1 mg/mL

Standard solution 1 mg/mL

Solution No.	Volume of sample(mL)	Volume of water(mL)	Volume of standard(mL)	Analyte Concentration		Instrument Reading (units)
				from sample (estimate)	from standard	
1	4.0	1.0	0.0	0.4	0.0	110-10* = 100
2	4.0	0.2	0.8	0.4	0.8	310-10 = 300
3	4.0	0.4	0.6	0.4	0.6	260-10 = 250
4	4.0	0.5	0.5	0.4	0.5	235-10 = 225
5	4.0	0.6	0.4	0.4	0.4	210-10 = 200

Extrapolation of calibration plot gives an intercept of 0.4 mg

Sample contains 0.4 mg/4 mL aliquot = 0.1 mg/mL

= 100 ppm

* 10 is the background contribution

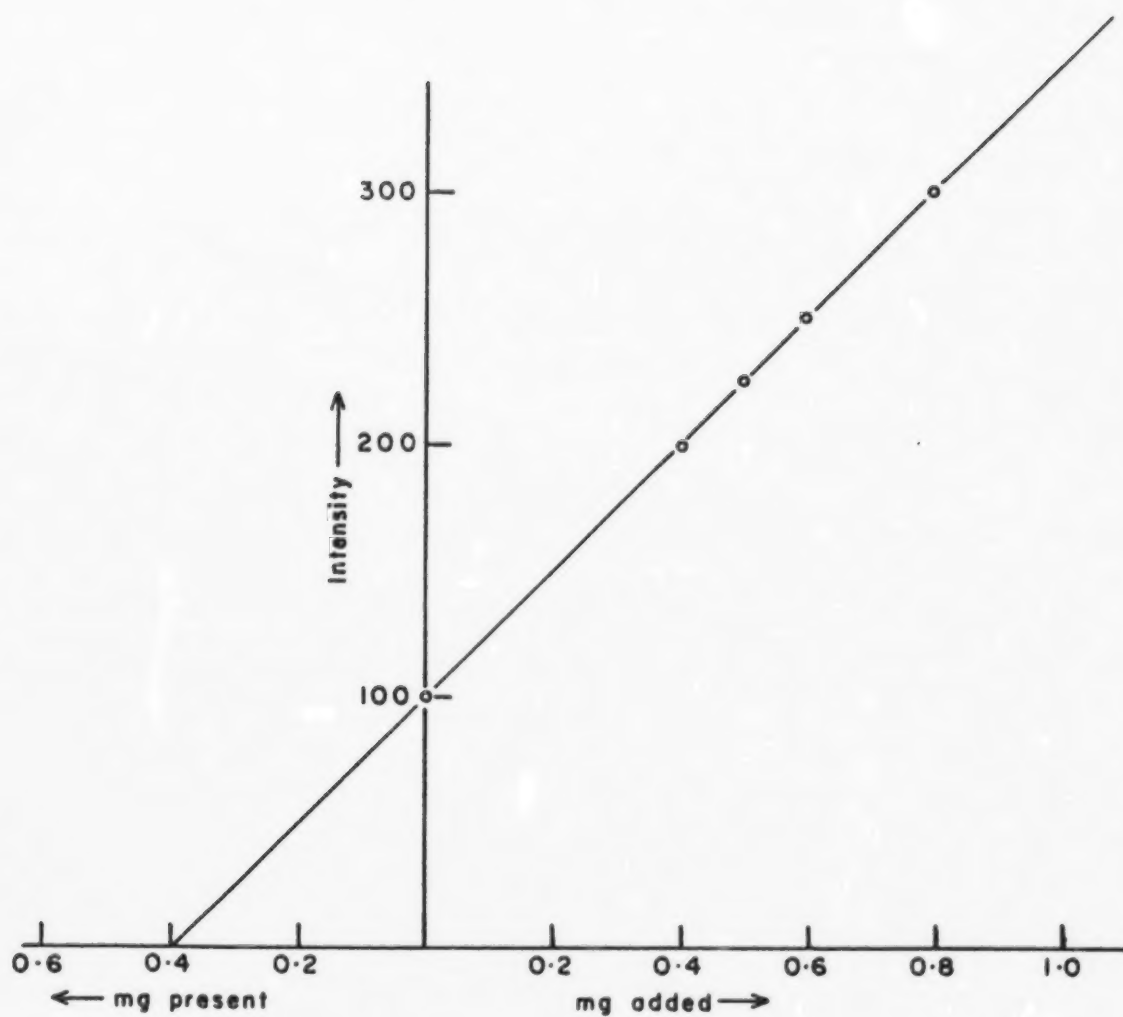


Fig. 1 — Standard Addition Plot